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CATALYTIC ALKYLATION OF BENZENE WITH ETHANOL AND PROPANOLS

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[Numbers in parentheses refer to appended bibliography.]

The few studies that have appeared on the catalytic alkylation of benzene with alcohols have dealt with the alkylation of benzene with methanol or ethanol in the gaseous phase at normal pressure. When the reaction takes place under these conditions, the yield of ethylbenzene, according to the literature (1), reaches 12-15 percent of the alcohol used in the reaction. Data on the alkylation of benzene with propanols can be found only in the patent literature.

In the present work we studied the possibility of alkylating benzene with ethanol or propanols with the use of an aluminum silicate catalyst under atmospheric pressure in a circulating system, i.e., a system in which a flow of the reacting substances is maintained.

The study made it clear that the yield of ethylbenzene in alkylating benzene with ethanol is a function of the volume rate of flow of the reaction mixture. With a volume rate of 0.03, the yield of ethylbenzene is 28 percent based on the alcohol; with a volume rate of 0.18, the yield is 25 percent; and with a volume rate of 0.66, the yield is 15 percent. The yield of ethylbenzene may be doubled by using the waste gases consisting mainly of ethylene.

In the alkylation of benzene with n-propanol or isopropanol (at a volume rate of flow equal to 0.66), isopropylbenzene is obtained in a yield of 49-54 percent. If the volume rate is reduced, the yield of isopropylbenzene is lowered because of the simultaneous occurrence of the reaction of dealkylation. As in the case of the alkylation of benzene with ethanol, the yield of isopropylbenzene may be increased by using the waste gases consisting mainly of propylene. Thus the feasibility of obtaining satisfactory yields of ethylbenzene and isopropylbenzene in a circulating system under normal pressure was established. One should remember that, under the conditions of our experiments, and based on the alcohol used in the reaction, the maximum possible yield (theoretically) of ethylbenzene is 85 percent; and of isopropylbenzene, 87 percent.

From the results obtained, several considerations can be advanced as to the mechanism of this particular reaction. We presume that the alkylation of benzene with alcohols does not proceed as a direct condensation of benzene with alcohol (benzene + alcohol → alkylbenzene + water), but with a preliminary dehydration of the alcohol. The activated olefin, formed in the reaction, reacts with benzene giving alkylbenzene (olefin + benzene → alkylbenzene). Such a reaction mechanism is confirmed by the ease of the formation of olefins from alcohols even at the point of complete "poisoning" of the catalyst for the alkylation reaction, by the high olefin content of the waste gases, by the suitability of the latter for alkylating benzene, and finally by the formation of isopropylbenzene in the alkylation of benzene with n-propanol. The assumption of the formation of isopropylbenzene by isomerization of n-propylbenzene is refuted from thermodynamic considerations, since at the temperature at which our experiments were carried out, the equilibrium isopropylbenzene ⇄

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n-propylbenzene favored the formation of n-propylbenzene. Thermodynamic calculation of the given reaction, and also of the dehydration reactions of alcohols and of the alkylation of benzene with alcohols and olefins, was based on the data of V. V. Korobov and A. V. Frost (2). However, a final decision as to the reaction mechanism in the alkylation of benzene with alcohols can be arrived at only by applying precise physicochemical methods.

EXPERIMENTAL DATA

Serving as starting materials were technically distilled and dried benzene (containing thiophene), absolute commercial ethanol with a bp of 77.5°C /738 mm, $n_D^{20} = 1.3605$, $d_4^{20} = 0.7889$; absolute n-propanol with a bp of 95-97°C /750 mm, $n_D^{20} = 1.3860$, $d_4^{20} = 0.8040$; and absolute isopropanol with a bp of 81-82°C /750 mm, $n_D^{20} = 1.3776$, $d_4^{20} = 0.7855$.

The alkylation reaction was conducted in the presence of an aluminum silicate catalyst of the industrial type in the usual apparatus for the circulation [flow] method. The gaseous reaction products were analyzed in the VTI (All-Union Thermal Engineering Institute) apparatus. Under optimum conditions the gases consisted of 98-99 percent of the corresponding olefins; the carbon dioxide content did not exceed 0.5 percent; and carbon monoxide, hydrogen, and saturated hydrocarbons were not found in the gases. In the work, we investigated the yield of the alkylbenzene as a function of the temperature of the experiment, the composition, and the speed of the passage of the reaction mixture [See appended figures 1, 2, and 3].

It is evident from the curves [shown in the appended figures] that at 450°C for a molar ratio of benzene to ethanol of 3:1 and a volume rate of flow equal to 0.03, the yield of ethylbenzene reached 28 per cent; with a volume rate of 0.18, the yield percent was 25; and for a rate of 0.66, 15 percent, based on the alcohol introducted into the reaction.

The dried product of catalysis, obtained under the conditions indicated, was distilled in the temperature range of 78-150°C. The ethylbenzene fraction (130-140°C) was investigated in more detail. This ethylbenzene fraction was found to have the following constants: bp of 135-136°C /757 mm, n_D^{20} - 1.4965, and $d_4^{20} = 0.8666$. The concentration of the ethylbenzene was 92-95 percent. The data obtained by distillation were confirmed by analysis of the fraction using the Raman light-dispersion method. (We wish to thank Ye. G. Treshchova, who carried out the spectrographic analyses.)

The optimum conditions for the alkylation of benzene with isopropanol were as follows: temperature of about 325°C; volume rate of flow of the reaction mixture, 0.66; molar ratio of the reacting components, i.e., of benzene to isopropanol, 4:1. The yield of isopropylbenzene under these conditions was 54 percent based upon the alcohol introduced into the apparatus.

The isopropylbenzene isolated from the isopropylbenzene fraction (144-145°C) obtained by distillation of the catalyzate (bp of 78-204°C) was found to have the following constants: bp of 151.5°C /760 mm, $n_D^{20} = 1.4922$, $d_4^{20} = 0.8599$, and purity of 96-98 percent. The content of isopropylbenzene in the fraction investigated was confirmed by the Raman light-dispersion method of analysis.

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Reduction of the rate of delivery of the reaction mixture reduces the yield of isopropylbenzene; for example, by passing the mixture of benzene/isopropanol with a volume rate of 0.18, a yield of only 45 percent was obtained. This is explained by the fact that simultaneous dealkylation of the isopropylbenzene takes place. We were convinced of this fact by the results of special experiments conducted and by the agreement of our findings with data found in the literature (3). As an example, on passage of isopropylbenzene over the catalyst at a volume rate of 0.18 at 325°C, the isopropylbenzene is dealkylated to the extent of approximately 13 percent into benzene and propylene.

Under these conditions, due to the rearrangement of the radicals in the reactions, 10 percent of the isopropylbenzene are converted simultaneously into benzene and diisopropylbenzene, the last forming a fraction with a bp of 197-204°C, n_D^{20} = 1.4920, and d_4^{20} = 0.8582. According to the data found in the literature 1,2-diisopropylbenzene (4) has a bp of 203.7°C, n_D^{20} = ~~1.4960~~, d_4^{20} = 0.8701; 1,3-diisopropylbenzene (5) has a bp of 203°C, n_D^{20} = 1.4884, d_4^{20} = 0.8566; and 1,4-diisopropylbenzene (5) has a bp of 210.3°C, n_D^{20} = 1.4895, d_4^{20} = 0.8571.

By carrying out the alkylation reaction at higher volume rates, dealkylation and rearrangement of the radicals are suppressed.

In the alkylation with n-propanol, the optimum conditions for the reaction are the same as for the alkylation with isopropanol. Isopropylbenzene also appears in the reaction product, but its yield is lower, (48-49 percent).

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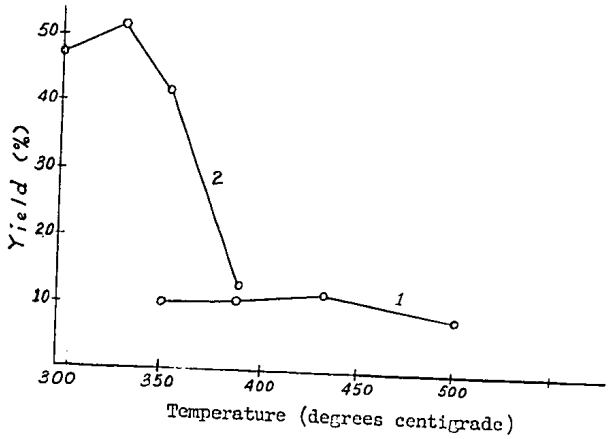

Figure 1. Yield of Alkylbenzene As a Function of Temperature

1. $C_6H_6 + C_2H_5OH$ (3:1), Volume Rate, 0.66
2. $C_6H_6 + i - C_3H_7OH$ (4:1), Volume Rate 0.66

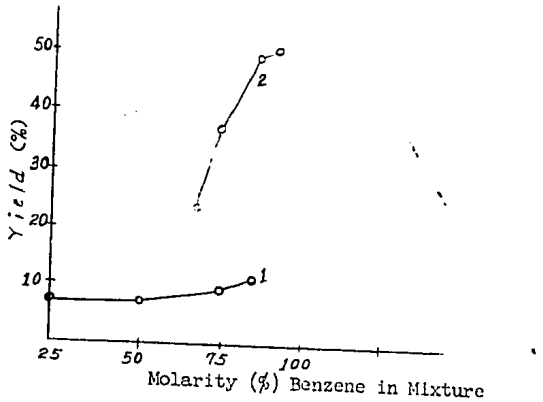

Figure 2. Yield of Alkylbenzene As a Function of Benzene Content in the Initial Mixture

1. $C_6H_6 + C_2H_5OH$, Temperature, 450°C, Volume Rate, 0.66
2. $C_6H_6 + i - C_3H_7OH$, Temperature, 325°C, Volume Rate, 0.66

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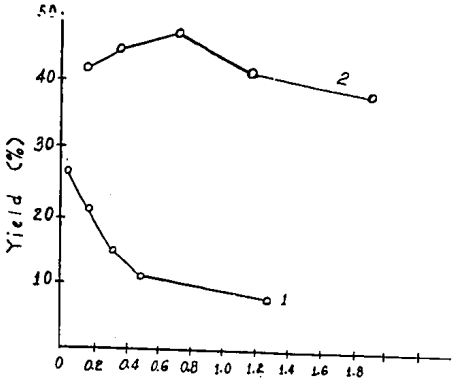

Figure 3. Yield of Alkylbenzene As a Function of Volume Rate of Passing the Initial Mixture

1. $C_6H_6 + C_2H_5OH$ (3:1), Temperature, 450°
2. $C_6H_6 + i\text{-}C_3H_7OH$ (4:1), Temperature, 325°

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